Polyetherimide/Dicyanate Semi-interpenetrating Polymer Networks Having a Morphology Spectrum†

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Abstract: The morphology, dynamic mechanical behavior and fracture behavior of polyetherimide (PEI)/dicyanate semi-interpenetrating polymer networks (semi-IPNs) with a morphology spectrum were analyzed. To obtain the morphology spectrum, we dispersed PEI particles in the precured dicyanate resin containing 300 ppm of zinc stearate catalyst. The semi-IPNs exhibited a morphology spectrum, which consisted of nodular spinodal structure, dual-phase morphology, and sea-island type morphology, in the radial direction of each dispersed PEI particle due to the concentration gradient developed by restricted dissolution and diffusion of the PEI particles during the curing process of the dicyanate resin. Analysis of the dynamic mechanical data obtained by the semi-IPNs demonstrated that the transition of the PEI-rich phase was shifted toward higher temperature as well as becoming broader because of the gradient structure. The semi-IPNs with the morphology spectrum showed improved fracture energy of 0.3 kJ/m², which was 1.4 times that of the IPNs having sea-island type morphology. It was found that the partially introduced nodular structure played a crucial role in the enhancement of the fracture resistance of the semi-IPNs.

Keywords : dicyanate, toughening, morphology, semi-IPNs, gradient.

Introduction

The toughening of thermoset materials using high performance thermoplastic has recently received attention because the toughened thermosets usually possess good thermal and mechanical properties. Improved fracture resistance in ther¬moplastic-modified thermosets has usually been obtained by introducing a secondary phase into the thermoset material via reaction induced phase separation, since homogeneous miscible systems have not exhibited a significant increase in fracture resistance.¹ For this purpose, rigid and thermally stable thermoplastics such as polysulfone,² ⁴ polyetherimide (PEI),⁵ ⁷ and polyethersulfone⁹ frequently have been used. In these systems, the thermoplastics are initially soluble in

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generation of a continuous thermoplastic phase.\textsuperscript{10,11}

To overcome these drawbacks, we introduced “a morphology spectrum concept” to the thermoplastic modified thermoset materials that has been described in previous papers.\textsuperscript{12,13} To obtain the morphology spectrum, we inserted a soluble thermoplastic film into neat thermoset resin, controlled the relative rate of the dissolution and diffusion of the inserted film, and controlled the curing reaction. The fully cured thermoset resin revealed three different types of morphology along the thickness direction because of the thermoplastic concentration gradient formed: co-continuous nodular structure where the concentration of thermoplastic was 20\% or more, sea-island type morphology where the concentration of thermoplastic was 10\% or less, and dual-phase morphology having both co-continuous nodular structure and sea-island morphology where the thermoplastic concentration was around 15\%. The semi-IPNs having a morphology spectrum exhibited improved fracture toughness as well as improved mechanical and thermal properties with a low overall content of thermoplastic. The morphology spectrum system prepared by inserting thermoplastic film, however, has an anisotropic character, which means that the fracture properties for loading in the direction of the thermoplastic film is greater than that for the transverse loading. Therefore, it is necessary to develop a new technical route for the morphology spectrum formation for general application.

The objective of this study was to explore a novel route for the morphology spectrum formation by dispersion of thermoplastic particles and to find the proper reaction conditions. This was attempted by using a zinc stearate catalyst and also by precurrying the thermoset resin before adding the thermoplastic particles. For this study, we prepared PEI/dicyanate semi-IPNs by the dispersion of the preformed PEI particles. Also, the dynamic mechanical properties and fracture behaviors of the semi-IPNs were investigated and compared with the control semi-IPNs having uniform morphology.

**Experimental**

**Materials.** Bisphenol-A dicyanate (AroCy B-10, Ciba-Geigy) was supplied as a white, high-purity (>99.5 \%) crystalline powder (melting point: 79\°C). The cyclotrimerization of the dicyanate resin is shown in Scheme I. A zinc stearate (ZnSt) catalyst was used to control the reaction rate of the dicyanate resin. Polyetherimide (Ultem 1000, General Electric Co., $M_\ell = 18,000$) (PEI) was used as the thermoplastic component. All materials were used as received from the manufacturer.

**Specimen Preparation.** The PEI/dicyanate semi-IPNs with a morphology spectrum were prepared by dispersion of PEI particles in precured dicyanate resin. In order to prepare PEI particles, the PEI pellets were first dissolved in chloroform to obtain a 4 wt\% solution. The solution was sprayed in air through a nozzle at room temperature. The residual solvent of the air-dried PEI particles was removed at 150\°C for 4 hr under vacuum. The particles were sieved to obtain relatively uniform particle size. The effective diameter of the particles measured by particle size analyzer (PAMAS system 2120) was 68.8 $\pm$ 13.8 $\mu$m. Dicyanate resin with 300 ppm of ZnSt catalyst was precured in an air-convection oven at 180\°C. For this study, four precure conversions (0, 0.25, 0.45, and 0.5) were selected from the dicyanate reaction kinetic data.\textsuperscript{10} The prepared PEI particles were added to the precured dicyanate resin and dispersed uniformly by a magnetic spin bar at 180\°C for 30 sec. Subsequently, the mixture was poured into an aluminum mold with dimensions of $70 \times 70 \times 2.5$ mm, and cured at 180\°C. The total curing time was 6 hr. Post curing was performed in the convection oven at 280\°C for 1.5 hr. The samples were designated as P$X$ where $X$ represents precure conversion. For example, P0 and P45, represent the precure conversions zero and 45\%, respectively. The overall composition of the PEI for this study was 7.5 wt\% in the dicyanate resin.

For comparison, a controlled sample with uniform concentration was also prepared by conventional solution-mixing techniques.\textsuperscript{8} The PEI was dissolved in methylene chloride and mixed with dicyanate resin with 300 ppm of ZnSt catalyst at room temperature. Most of the solvent was evaporated on a hot plate at 40-60\°C and the residual solvent was removed under vacuum conditions at 100\°C for 1.5 hr. The PEI/dicyanate mixture was cured under the same curing conditions.

**Measurements.** The dynamic mechanical measurement was performed by using a dynamic mechanical thermal analyzer (Rheometrics Scientific DMTA IV) in dual-cantilever bending mode. The dimension of the samples for the test was $35 \times 10 \times 2$ mm. The measurements were made at a fixed frequency of 1 Hz with a heating rate of 2\°C/min over a temperature range of 50 to 350\°C.

The morphologies of the cured resins were examined using a scanning electron microscope (Philips XL30S). The fractured surfaces of post-cured samples were coated with a thin layer of a gold-palladium alloy. To observe the cross-section of the dried PEI particles before dispersion, the particles were first dispersed in a phenolic resin (resol type),

**Scheme I.** Molecular structure of the dicyanate monomer and the trimerization reaction involved during cure.